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Air Sampling and Analysis Method for Volatile Organic Compounds (VOCs) Related to Field-Scale Mortality Composting Operations

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In biosecure composting, animal mortalities are so completely isolated during the degradation process that visual inspection cannot be used to monitor progress or the process status. One novel approach is to monitor the volatile organic compounds (VOCs) released by decaying mortalities and to use them as biomarkers of the process status. A new method was developed to quantitatively analyze potential biomarkers—dimethyl disulfide, dimethyl trisulfide, pyrimidine, acetic acid, propionic acid, 3-methylbutanoic acid, pentanoic acid, and hexanoic acid—from field-scale biosecure mortality composting units. This method was based on collection of air samples from the inside of biosecure composting units using portable pumps and solid phase microextraction (SPME). Among four SPME fiber coatings, 85 μ m CAR/PDMS was shown to extract the greatest amount of target analytes during a 1 h sampling time. The calibration curves had high correlation coefficients, ranging from 96 to 99%. Differences between the theoretical concentrations and those estimated from the calibration curves ranged from 1.47 to 20.96%. Method detection limits of the biomarkers were between 11 pptv and 572 ppbv. The applicability of the prepared calibration curves was tested for air samples drawn from field-scale swine mortality composting test units. Results show that the prepared calibration curves were applicable to the concentration ranges of potential biomarker compounds in a biosecure animal mortality composting unit.

KEYWORDS: Air sampling; compost gas; GC-MS; dimethyl disulfide; dimethyl trisulfide; SPME; volatile fatty acids

INTRODUCTION

The development of new analytical techniques for volatile organic compounds (VOCs) emitted from animal production operations is an increasingly important public and regulatory issue. Composting is widely accepted as an on-farm treatment and disposal method for animal mortalities and is useful for daily management and in emergency animal disease outbreaks (1). In biosecure composting applications (2, 3), mortalities are completely covered in an envelope containing large amounts of plant materials (e.g., straw, wood shavings/chips, old hay) and additional plastic barriers. The plastic barrier (e.g., tarp or wrap) and the thickness of the envelope plant material layers prevent the monitoring of the decomposition or decay of mortalities by visual inspection. Thus, an alternative assessment method for the completion of the animal tissue decay process is needed.

An understanding of the volatiles released during the animal mortality composting processes could provide useful insights in

determining the status and completion of carcass degradation. Moreover, the composition of the compost exhaust air indicates the aeration status of the process and the quality of the final product (4, 5). Previous research identified the probable biomarker gases released by swine mortalities inside biosecure compost systems (6–8) as dimethyl disulfide (DMDs), dimethyl trisulfide (DMTS), and pyrimidine. Light molecular weight volatile fatty acids (VFAs) were also found in significant amounts and are known to be associated with anaerobic degradation during composting, along with products of carbohydrate fermentation (9), which are indicative of plant envelope material degradation.

Sampling and analyzing air from composting operations are challenging due to the reactive and polar properties of target (potential biomarker) VOCs. Conventional air sampling methods use sorbent tubes, impingers, and vacuum canisters and often focus on specific functional groups of chemical compounds separately. These methods require costly equipment, lengthy sample collection and preparation periods, and complicated extraction procedures. Solid phase microextraction (SPME) offers many advantages for air sampling, such as high precision

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compound	CAS Registry No.	MW ^a	formula	density ^b (g/mL)	solubility in ethanol	vapor pressure ^c (kPa)
dimethyl disulfide	624-92-0	94.20	C ₂ H ₆ S ₂	1.062	soluble ^d	3.0
dimethyl trisulfide	3658-80-8	126.26	C ₂ H ₆ S ₃	1.202	soluble	0.8
pyrimidine	289-95-2	80.08	C ₄ H ₄ N ₂	1.016	soluble	2.0
acetic acid	64-19-7	60.05	C ₂ H ₄ O ₂	1.049	miscible	1.5
propanoic acid	79-09-4	74.07	C ₃ H ₆ O ₂	0.980	miscible	0.3
3-methylbutanoic acid	503-74-2	102.13	C ₅ H ₁₀ O ₂	0.931	miscible	0.2
pentanoic acid	109-52-4	102.13	C ₅ H ₁₀ O ₂	0.933	soluble	0.02
hexanoic acid	142-62-1	116.15	C ₆ H ₁₂ O ₂	0.920	soluble	0.02

Before the experiments were begun, the standard gas generation system was tested for (1) the possibility of condensation, (2) accuracy of the syringe pump, (3) homogeneous mixing, (4) adsorption to walls, and (5) reactions between analytes. The highest concentrations used to prepare calibration curves (**Table 2**) were used for these tests to challenge SPME for possible competitive adsorption and limits of sorptive capacity. The possibility of condensation, adsorption to walls, and reactions between

Table 2. Calibration Curves with Correlation Coefficients, Concentration Ranges of the Calibration Curves (Seven Data Points), and Relative Standard Deviations (RSDs) of the Concentrations Used for Calibrations

compound	calibration curves		concn range (ppmv)	RSD range (%)
	dry conditions	humid conditions		
dimethyl disulfide	$y = 1.78 \times 10^7 x - 6.17 \times 10^4$ $R^2 = 0.998$	$y = 1.74 \times 10^7 x - 8.75 \times 10^4$ $R^2 = 0.998$	0.01–6.85	1.20–4.15
dimethyl trisulfide	$y = 1.51 \times 10^7 x - 3.33 \times 10^6$ $R^2 = 0.990$	$y = 1.46 \times 10^7 x - 2.86 \times 10^6$ $R^2 = 0.990$	0.02–5.95	1.07–4.73
pyrimidine	$y = 2.08 \times 10^7 x + 4.47 \times 10^6$ $R^2 = 0.976$	$y = 2.03 \times 10^7 x + 3.49 \times 10^6$ $R^2 = 0.979$	0.03–6.25	0.24–7.16
acetic acid	$y = 5.17 \times 10^6 x - 1.54 \times 10^6$ $R^2 = 0.993$	$y = 4.78 \times 10^6 x - 2.46 \times 10^6$ $R^2 = 0.986$	0.20–15.6	0.96–11.4
propanoic acid	$y = 9.92 \times 10^6 x - 4.87 \times 10^6$ $R^2 = 0.967$	$y = 8.50 \times 10^6 x - 3.20 \times 10^6$ $R^2 = 0.972$	0.16–13.2	0.72–14.8
3-methylbutanoic acid	$y = 2.24 \times 10^7 x - 9.09 \times 10^5$ $R^2 = 0.985$	$y = 2.07 \times 10^7 x - 3.56 \times 10^6$ $R^2 = 0.984$	0.11–6.12	0.57–11.2
pentanoic acid	$y = 2.51 \times 10^7 x - 2.81 \times 10^5$ $R^2 = 0.995$	$y = 2.30 \times 10^7 x - 8.03 \times 10^5$ $R^2 = 0.990$	0.11–7.24	0.40–7.26
hexanoic acid	$y = 2.32 \times 10^7 x - 1.94 \times 10^6$ $R^2 = 0.991$	$y = 2.28 \times 10^7 x - 2.55 \times 10^6$ $R^2 = 0.991$	0.09–5.54	0.47–12.4

Table 3. Comparison of Theoretical and Measured Concentrations and Method Detection Limits (MDL^a) for Dry and Humid Air Conditions

compound	C_{analyte} (theory, ^b ppbv)	measured C_{analyte} (SPME, ppbv)					
		at dry conditions			at humid conditions		
		av ^c	% diff ^d	MDL ppbv	av ^c	% diff ^d	MDL ppbv
dimethyl disulfide	28	30 A ^e	7.14	1	27 A	3.57	1.1
dimethyl trisulfide	23	20 A	13.04	5.7	19 A	17.39	5.5
pyrimidine	2	2.1 A	0.50	0.01	2 A	0.00	0.011
acetic acid	430	789 A	9.30	520	765 B	12.09	551
propanoic acid	610	631 A	3.44	580	601 B	1.47	572
3-methylbutanoic acid	225	251 A	11.55	120	233 B	3.55	180
pentanoic acid	229	195 A	14.87	40	181 B	20.96	36
hexanoic acid	197	210 A	6.59	110	202 A	5.00	120

^a Ten measurements were made for each MDL value presented. ^b Theoretical concentrations calculated based on standard gas generation rates. ^c Measured concentrations calculated from the calibration curves. ^d Percent difference between the theoretical and measured concentrations. ^e Means within a column that are not followed by the same letter are significantly different.

analytes was tested for both dry (0% RH) and humid (97% RH) conditions.

In the study, the injection T port was not heated, and because of this, the possibility of condensation inside the T was checked. For this purpose, the mixing T was replaced with a glass sampling bulb, and air with standard analytes was allowed to pass through for 2 h (average run time of the syringe pump). The glass bulb was then washed with ethanol. This washed ethanol was directly injected into the GC. None of the compounds were found in the ethanol wash. It is concluded that if there is no condensation after 2 h of testing time, then there will not be any significant condensation in the system. This finding was also supported with visual inspection of the glass sampling bulbs.

The accuracy of the syringe pump delivery rate was confirmed through two approaches. In the first, the preweighed syringe was used to deliver a mixture of VOCs for a period of time. The pump delivery rate was calculated on the basis of the weight difference ($n = 5$). In the second approach, the volume difference was recorded and the delivery rate was calculated on the basis of this difference ($n = 5$). The relative standard deviation of these 10 measurements was 0.19%. Only a 0.014% difference was found between the theoretical delivery rate and the delivery rates calculated from these two approaches.

The homogeneous mixing of air and standards before the sampling port (situated in the third glass sampling bulb) was also tested. The preliminary experiments showed that when only three glass sampling bulbs were used, homogeneous mixing was not achieved before the third glass bulb. Thus, 6 mm diameter Pyrex glass beads (113 g, Fisher Scientific, Pittsburgh, PA) were used to improve the mixing (Figure 1). A U-shape tube was filled with glass beads and connected to the first glass sampling bulb. After this

modification, standards were extracted from the second and third glass sampling bulbs. No significant difference was found between the MS detector response of standards from the second and third sampling bulbs. It was concluded that using glass beads resulted in homogeneous mixing of the standards before the VOCs reach the sampling port.

The possibility of adsorption to the walls in the standard generation system was also tested. Before sampling, the system was run for 1 h to reach equilibrium and to minimize wall adsorption effects. To test equilibrium conditions, samples were collected from the second and third sampling bulbs after the system had been run for an hour. Results show that there is no significant difference between the MS detector response of standards from the second and third sampling bulbs and that 1 h is enough to reach equilibrium.

The possibility of reactions between analytes in a gas standard sample was tested by directly injecting the mix into the injection port of the GC. The concentrations reported in Table 3 (theoretical concentrations) were used in this experiment. No formation of new compound was detected.

SPME Fiber Selection. Four commercially available SPME fibers were compared in a 1 h extraction time by evaluating peak area values, that is, the amount of the analytes extracted by the fibers (25). The tested fibers were 85 μm carboxen/polydimethylsiloxane (CAR/PDMS), 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), and 85 μm polyacrylate (PA) (Supelco, Bellefonte, PA). This selection was based on a literature review and previous experience with target analytes. New SPME fibers were first conditioned according to the manufacturer's directions. In addition, SPME fibers were inserted into the injection port of the GC for 5 min to thermally desorb impurities on the

fiber immediately before sampling. All of the GC-MS conditions were the same for all fibers tested.

Sampling Time Selection. The practical sampling time was optimized for the 85 μm CAR/PDMS fiber coating. Sampling times of 1, 3, 10, 60, 360, and 720 min were tested. Because CAR/PDMS is an adsorptive-type fiber coating, analytes were extracted under nonequilibrium conditions. The sampling time was chosen as the longest practical time for linear extraction (mass extracted vs sampling time) that does not result in competitive extraction under the worst-case scenario (i.e., highest observed concentrations of target analytes in field samples).

Demonstration of the Quantitative Analysis. An example of the quantitative analysis of target VOCs was demonstrated for air samples collected from field-scale swine mortality composting units. Details of the composting units were described in previous publications (25, 26). On the 10th day of the process, air samples were drawn from the center location of the composting units using SKC pumps (model 224-PCXR4, Bellefonte, PA). It is generally known that VOC production is most intense in the first 10 days of a composting process (8, 27). This intense VOC production period was selected to collect VOC samples to show the applicability of the developed calibration curves for the possible highest concentrations of VOCs. The applicability of the calibration curves for the lowest concentrations is shown by method detection limits. Air samples were captured inside a single 250 mL glass sampling bulb. The air flow rate during sampling was 1.0 L/min, and the sampling start time was 5 min (20 hydraulic residence times) to allow the system to reach steady state conditions. VOCs were sampled using the selected SPME fiber and sampling time.

Sample Analysis. All gas analyses were performed using an integrated multidimensional 6890N GC and 5973 MS system assembled by Microanalytics (Round Rock, TX) based on the Agilent Inc. (Wilmington, DE) platform. Ultrahigh-purity (99.995%) helium was used as the carrier gas at constant pressure mode. The injector and SPME fiber desorption temperatures were 260 °C. The initial temperature of the GC oven was 40 °C with a 3 min holding time, followed by a ramp of 10 °C/min to 220 °C, at which it was held for 10 min. Two capillary columns connected in series were used to separate compounds. The precolumn was a 12 m \times 0.53 mm BP5 with an inside diameter (i.d.) of 0.25 μm , and the analytical column was a 25 m \times 0.53 mm i.d. \times 0.25 μm BP20 (both from SGE, Austin, TX). The heart-cut valve between the precolumn and analytical column was opened between 0.05 to 28 min, and the backflush of the precolumn was activated between 28 and 31 min to prepare the system for the following run. The MS mass/charge (m/z) ratio was set between 33 and 150 for the first 8 min. After that, the MS m/z ratio was between 34 and 280. The transfer line, quadrupole, and MS source temperatures were 240, 150, and 230 °C, respectively. The standard gas method detection limit (MDL) was calculated at the 99% confidence level for a signal-to-noise ratio of 5 and a standard deviation of 10 replicate measurements (24).

Data Analysis. Chromatography data acquisition software consisting of MSD ChemStation (Agilent, Wilmington, DE) and BenchTop/PBM V. 3.2.4 (Palisade Corp., Ithaca, NY) was used to analyze data. Separated compounds were identified using mass spectral matches with ChemStation's NIST MS and PBM Benchtop MS libraries. Spectral matches and column retention times were compared with those of standard analytes.

Statistical Analysis. Experiments were run in triplicate ($n = 3$). All data were analyzed using the statistical package JMP v. 6.0.2 (SAS Institute, Inc., Cary, NC). Data were subjected to a one-way analysis of variance (ANOVA). Treatment means were compared using Tukey's honestly significant difference (HSD) test at the 95% confidence level. Correlation coefficients of the calibration curves were calculated using Excel tools.

RESULTS

Fiber Selection. The optimized SPME fiber coating was selected on the basis of a comparison of the amount of analyte SPME fibers extracted in a 1 h sampling time (Figure 2). The concentrations ranged from 2.81 ppmv for hexanoic acid to 7.9 ppmv for acetic acid. These concentrations were in the middle range of the calibration curves. The relative standard deviations (RSDs) ranged from 1 to 9%. The 85 μm CAR/PDMS fiber

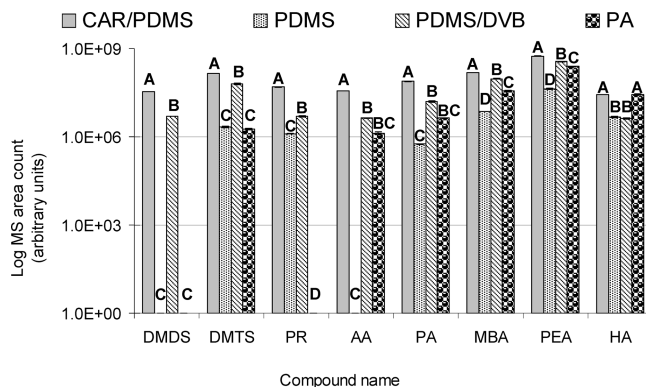


Figure 2. Extraction efficiencies of different SPME fiber coatings (SPME at room temperature and in a 1 h extraction time). Means (within a compound) that are not associated with the same letter are significantly different; $n = 3$; $p \leq 0.05$.

provided the highest extraction efficiency and was found to be statistically significantly different in comparison with the other SPME fibers tested. On the basis of the amount of analytes extracted, efficiencies of the fibers were ranked from highest to lowest as CAR/PDMS > PDMS/DVB > PDMS \approx PA (Figure 2). These results can be explained by the characteristics of the fiber coatings as mixed phase coatings (CAR/PDMS and PDMS/DVB) having complementary properties compared to homogeneous phase coatings (PDMS and PA). Because the majority of interaction is determined by the adsorption process on a porous surface, CAR/PDMS and PDMS/DVB are suitable for more VOCs compared to PDMS and PA fiber coatings (28). Thus, DMDS, DMTS, pyrimidine, and VFAs were extracted at higher amounts by CAR/PDMS and PDMS/DVB compared to PDMS and PA (Figure 2). The DVB phase is mainly mesoporous and ideal for trapping C_6 – C_{15} analytes. Unlike DVB, CAR is microporous and traps C_2 – C_6 analytes (29). This explains the better extraction efficiency of CAR/PDMS compared to PDMS/DVB for the compounds ranging from C_2 to C_6 (Figure 2 and Table 1).

Extraction Time Selection. Carboxen/PDMS is an adsorptive SPME fiber coating and is susceptible to competitive adsorption if overloaded. Six extraction times were tested for this SPME fiber coating. The amounts of analytes extracted are shown in Figure 3. The RSDs of means ranged from 1 to 14%. For the 6 and 12 h extraction times, an increase in extraction time did not lead to a significant increase in the amount of analyte extracted (Figure 3). This was likely caused by the limited sorptive capacity of SPME. The 1, 3, 10, and 60 min sampling times were graphed separately (Figure 4), and the linearity of the response was evaluated. Correlation coefficients of the curves ranged from 96 to 99%. In a 1 h sampling time, there was no apparent displacement of the compounds, and 1 h was chosen as the proper sampling time for the CAR/PDMS fiber coating to quantify DMDS, DMTS, pyrimidine, and low molecular weight VFAs.

Calibration Curves and Method Detection Limits. The quantification of target VOCs was based on the calibration curves for the optimized 1 h sampling time. Calibration curves were prepared for both dry ($\sim 0\%$ RH) and humid ($\sim 97\%$ RH) air conditions (Table 2). The concentration ranges of the compounds and RSDs are shown in Table 2. The concentrations ranged from 0.01 to 6.85 ppmv for dimethyl disulfide and from 0.2 to 15.6 ppmv for acetic acid. The replicates had RSDs ranging from 0.32 to 5.01%. No significant difference in extraction efficiency was detected between dry and humid air conditions for DMDS, DMTS, pyrimidine, and hexanoic acid. However, significant

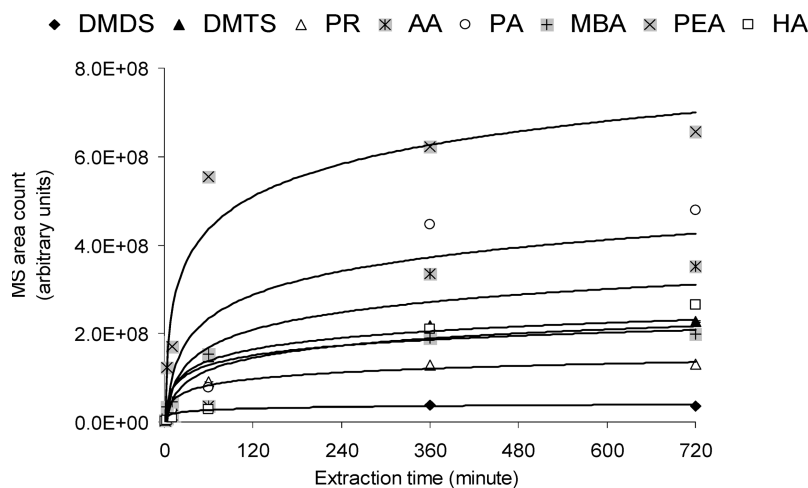


Figure 3. Extraction efficiencies in 1, 3, 10, 60, 360, and 720 min sampling times (85 μ m CAR/PDMS SPME fiber, room temperature).

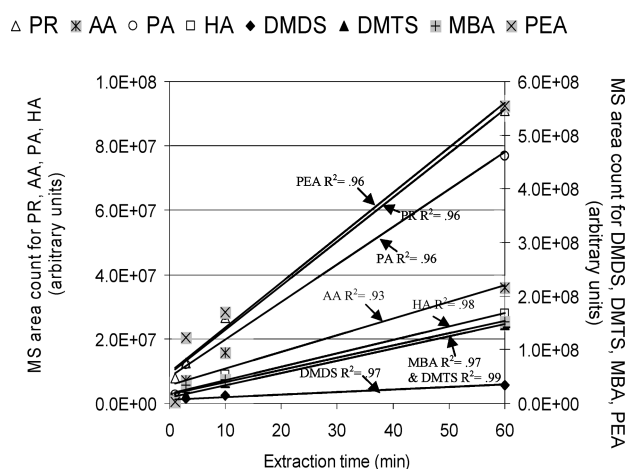


Figure 4. Extraction efficiencies in 1, 3, 10, and 60 min extraction times and correlation coefficients (85 μ m CAR/PDMS SPME fiber, room temperature).

differences were detected for acetic, propanoic, 3-methylbutanoic, and pentanoic acids at 97% RH conditions compared to dry air (0% RH) conditions. Lower concentrations of these acids were detected at 97% RH humid conditions compared to 0% RH dry conditions. This is important because in a typical swine mortality composting operation, air samples collected in the early stage of the process are expected to have a very high RH (approximately 100%). However, in further stages, compost materials lose some of their moisture and air samples have a RH ranging from 0 to 100%. If the RH of the air samples is not known, concentrations of the DMDS, DMTS, pyrimidine, and hexanoic acid can be calculated using either of the calibration curves. However, if the RH is not known, calculating exact concentrations of acetic, propanoic, 3-methylbutanoic, and pentanoic acids will not be possible. In this situation, a range of concentrations can be reported by using both the calibration curves prepared for dry (\sim 0% RH) and humid (\sim 97% RH) conditions.

The concentrations calculated on the basis of standard gas generation rates (theoretical concentrations) were compared with the measured concentrations estimated from the calibration curves (Table 3). The theoretical concentrations were chosen arbitrarily but were in the low range of concentrations considering the challenges of sampling and analysis at low concentrations.

The estimated concentrations from the field-scale composting units were all above MDLs (Table 3) and, thus, reliable. Measured concentrations were found to be different from the theoretical concentrations at levels ranging from 1.47 to 20.96%, which is within the range of differences reported between theoretical and measured *n*-alkane concentrations, 2–17% (22), and considered to be acceptable.

Application to Field Air Sampling. An example of a total ion chromatogram of the air samples drawn from field-scale swine mortality composting units is shown in Figure 5. VOC concentrations were calculated using both the calibration curves prepared for dry (\sim 0% RH) and humid (\sim 97% RH) conditions (Table 4). Gas concentrations of the compounds ranged from 0.06 to 7.39 ppmv. This is the typical range of concentrations measured from the biosecurity barriers of field-scale swine mortality composting units (8). These concentrations were lower than the high concentration range of the calibration curves, but higher than the MDLs. It is shown that the prepared calibration curves can be used for the concentration ranges detected from a field-scale composting unit. The developed method considers both the dry and humid conditions of the composting process and is applicable to quantitatively analyzing VOCs from field-scale swine mortality composting operations.

DISCUSSION

A new method was developed to quantitatively analyze DMDS, DMTS, pyrimidine, acetic acid, propanoic acid, 3-methylbutanoic acid, pentanoic acid, and hexanoic acid from field-scale mortality composting operations. The 85 μ m CAR/PDMS SPME fiber is shown to extract the highest amount of analytes in a 1 h sampling time. It is observed that in this sampling time there is no risk of analyte displacement for typical concentrations of target analytes. The prepared calibration curves have high correlation coefficients, ranging from 96 to 99%.

Measured concentrations were found to be different from the theoretical concentrations at a level ranging from 1.47 to 20.96%. These differences are within the range of differences reported between theoretical and measured *n*-alkane concentrations of 2–17% (22) and considered to be acceptable. No significant difference is found for DMDS, DMTS, pyrimidine, and hexanoic acid concentrations extracted under dry (0% RH) and humid (97% RH) conditions. However, lower concentrations of acetic acid, propanoic acid, 3-methylbutanoic acid, and pentanoic acid were detected at 97% RH conditions compared to dry conditions (0% RH). A range of these VOC concentrations can be calculated

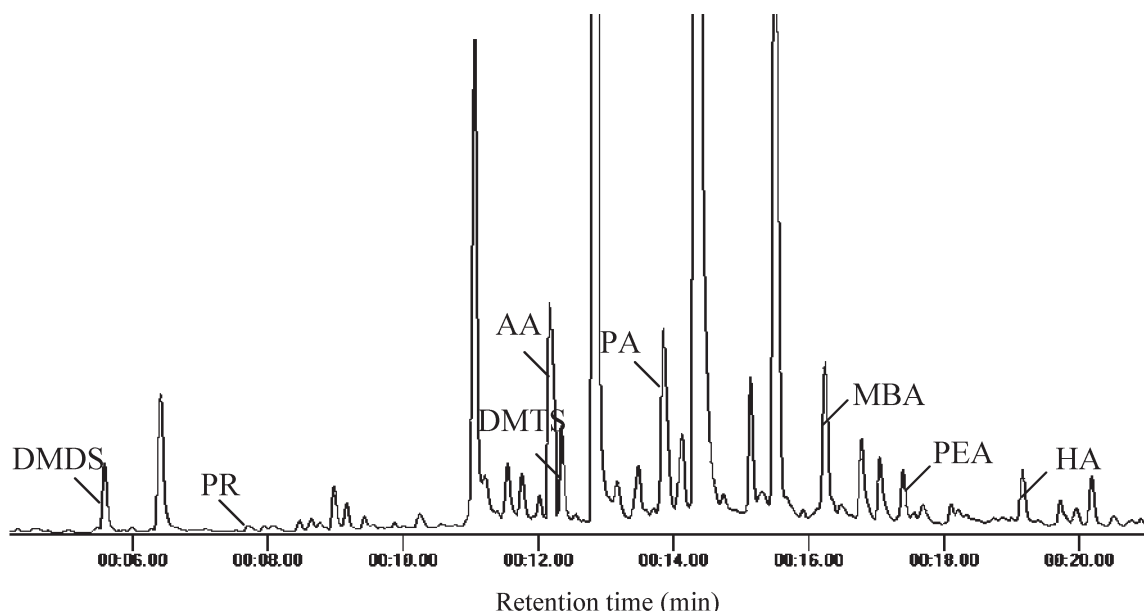


Figure 5. Total ion chromatogram of air sample collected from a field-scale swine mortality composting operation (85 μ m CAR/PDMS SPME fiber, 1 h sampling time, room temperature).

Table 4. Measured VOC Concentrations in Air Samples Collected from a Field-Scale Swine Mortality Composting Operation 10 Days after Construction

retention time ^a (min)	compound	MS area counts (arbitrary units)	concn (ppmv)	
			dry conditions	humid conditions
5.55	dimethyl disulfide	1.1×10^7	0.59	0.60
7.86	dimethyl trisulfide	4.7×10^6	0.07	0.06
12.10	pyrimidine	3.3×10^7	6.84	7.39
12.27	acetic acid	9.9×10^6	0.43	0.48
13.78	propanoic acid	2.3×10^7	2.76	3.02
16.17	3-methylbutanoic acid	1.9×10^7	0.88	1.08
17.34	pentanoic acid	8.5×10^6	0.35	0.41
19.10	hexanoic acid	1.2×10^7	0.64	0.66

^a GC column retention times and MS spectra of the compounds were matched with the standard analytes.

using the calibration curves prepared for dry (~0% RH) and humid (~97% RH) air conditions.

The applicability of the prepared calibration curves was tested for air samples drawn from a field-scale swine mortality composting unit. Results show that the calibration curves were valid for the highest possible concentrations (in the headspace) that can be measured from a field-scale composting operation. MDLs were found to range from 11 pptv (pyrimidine) to 572 ppbv (propanoic acid). SPME and standard gas generation using syringe pump injection are found to provide good estimates of the concentrations of DMDS, DMTS, pyrimidine, and VFAs. These techniques can be used for relatively rapid and sensitive quantitative analysis of VOCs from composting operations. The findings from this study could be used to develop sampling and quantification methods for other volatile organic compounds of the mortality composting operations. Other potential compounds of interest may include dimethyl sulfide, methanethiol, and ethanethiol.

ABBREVIATIONS USED

CAR/PDMS, Carboxen/polydimethylsiloxane; DMDS, dimethyl disulfide; DMTS, dimethyl trisulfide; GC, gas chromatography; MS, mass spectroscopy; PA, polyacrylate; PDMS, polydimethylsiloxane; PDMS/DVB, polydimethylsiloxane/divinylbenzene; PTFE, polytetrafluoroethylene; SPME, solid phase microextraction; VFA, volatile fatty acids; VOC, volatile organic compound.

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